Facile and Efficient Self-template Synthesis of Core-coronal-shell ZnO@ZIF-8 Nanohybrid Using Ascorbic Acid and its Application for Arsenic Removal

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In the present contribution, a facile and efficient protocol for synthesis a nanohybrid structure of core-coronal-shell ZnO@ZIF-8 using ascorbic acid (ZnO@AA/ZIF-8) as a new adsorbent for arsenic removal from water has been represented. For this purpose, the ZnO nanospheres were synthesized by a green and simple method followed by coating with ascorbic acid (AA) to modify their surface to achieve better growth of ZIF-8 on the surface of ZnO. After that, the core-coronal-shell ZnO@ZIF-8 nanohybrid obtained *via in situ* ZIF-8 formation using the dispersion of ZnO (as a core) in an ethanol solution only including 2-methylimidazole under moderate conditions. Here, ZnO is utilized as a template (core) as well as the metal node for ZIF-8 synthesis. The as-synthesized ZnO and ZnO@AA/ZIF-8 structures were characterized by different techniques such as XRD, FT-IR, TGA and, SEM-EDS. The analyses data confirmed the benefit of the method for the preparation of this new nanohybrid. The nanostructured ZnO@AA/ZIF-8 exhibited high efficiency in the removal of arsenic from water. The obtained results confirmed that core-coronal-shell metal oxide@MOF nanohybrid could be introduced asefficient candidates for heavy metalsremovalfor practical applications.

Keywords: Core-coronal-Shell, Ascorbic acid, Green synthesis, Dye degradation, ZIF-8

INTRODUCTION

To date, different types of metal oxides such as TiO_2, SnO_2, ZrO_2, CeO, MnO, Al_2O_3, FeO, ZnO, and binary metal oxides have been employed as an adsorbent for heavy metal removal from drinking and wastewaters [1,2]. Among these nano-oxometals, ZnO has been considered as a good candidate, owing to its low-cost raw materials, facile, and relatively fast synthesis, high thermal and good electrical and optical properties and so on [2]. Due to its surface hydroxyl groups, it can be a great candidate for immobilizing organo-chemical and biologic materials by coating the surfaces with a suitable linker for various applications [3]. Moreover, in current years, the development of core/shell structured materials over the metal oxide has been extensively investigated. Many studies have been accomplished on core/shell composites, which the ZnO nanoparticles plays a critical role as a core [4,5]. The core-shell systems can be used for different application such as absorbent for removal of heavy metal ions from wastewater such as lead, cadmium, mercury, arsenic [6]. Arsenic is inherently occurring as a heavy-ion in groundwater. The arsenic pollution in groundwater befalls due to different reasons such as combustion of fossil fuels, mining and metallurgical activities, and so on [7].

On the other hand, for arsenic removal *via* adsorption process by a certain adsorbent, having the high specific surface area and high specific affinity is essential. Although for metal oxides high specific affinity is usually occurred due to the presence of hydroxyl groups on metal oxides surfaces [1], almost all metal oxides suffer from their very low surface area [2]. For example, Kumar *et al*. in 2015 [2] reported only 15.75 and 24.48 m^2 g^{-1} for ZnO and SnO_2 specific surface area, respectively.

To efficiently improve the specific surface area of metal

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oxides, their incorporation with some porous materials such as metal-organic frameworks (MOFs), porous polymer networks (PPNs) and covalent organic frameworks (COFs) have attracted considerable attention [8-13]. Among these advanced porous materials, MOF materials especially zeolitic imidazolate frameworks (ZIFs) family with high specific surface area, high chemical stability, well-controlled pore sizes, and easier synthesis have been under plenty of attention [8-14]. This integration of MOFs and metal oxides is reachable through two procedures: a) deposition of metal oxides inside the pores of MOFs and b) surface coating of metal oxides using MOF materials as shell, which the latter is more common to reach core-shell nanohybrid structures [10].

For example, Yu *et al.*, in 2015 [10] synthesized a core-shell ZnO@ZIF-8 photocatalyst for methylene blue degradation under UV light. To control the appropriate growth of ZIF-8 on the surface ZnO, they used cetyltrimethylammonium bromide (CTAB) as a functional group. They concluded that the outer ZIF-8 shell in the ZnO@ZIF-8 photocatalyst is the main reason for improving the photocatalytic activity of ZnO in the presence of H_2O_2. Yang *et al.*, in 2018 [8] reported the facile synthesis of ZnO/ZIF-8 hybrid catalyst for rhodamine B (RhB) degradation. Their results revealed that the highest photocatalytic activity with 98.17% degradation of RhB after 12 min of UV light irradiation. At the same year, Cui et al., [11] encapsulated ZnO into the pores of ZIF-8 to achieve a core-shell ZnO@ZIF-8 structure. They showed the as-synthesized core-shell material efficiently enhances the performance for hydrogen sensing compared to pristine ZnO.

In this study, we incorporated 2-methylimidazole to ascorbic acid-coated ZnO nanopowders as a core to achieve a new heterogeneous nano absorbent. For this purpose, ZnO nanoparticles are synthesized and characterized by simple and novel method. Afterward, the core-shell ZnO@ZIF-8 nanohybrid is prepared using ascorbic acid as a specific functional group to control the growth of ZIF-8 on the surface of ZnO. The presence of ascorbic acid on the surface of ZnO not only prevents the direct nucleation of ZIF-8 in solution and assure the complete formation of the ZIF-8 shell but also creates new hydroxyl groups to improve specific affinity for arsenic removal (Scheme 1). Hence, this

nanohybrid structure, which is named as core-coronal-shell Zno@ZIF-8 (ZnO@AA/ZIF-8) benefits both advantages of high specific surface area and affinity simultaneously.

EXPERIMENTAL

Materials

All chemicals were used without purification; all the solutions were prepared in 18 MΩ cm⁻¹ double deionized water (DDW). Zinc nitrate hexahydrate (purity 99%), ethylene glycol (purity 99.8%), ascorbic acid (purity 99%) were purchased from Sigma-Aldrich Company, 2-methylimidazole (2-MIm) (purity 99%) were obtained from Sigma-Aldrich and was used for the formation of zeoliticimidazolate framework-8 (ZIF-8).

Instruments

Physicochemical properties of the catalyst was characterized by analytical methods such as powder X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), the catalyst morphology was examined using scanning electron microscopy (SEM) by an LEO VP-1450 equipped with an energy-dispersive X-ray (EDX), spectrometer and pH meter (Metrohm 827) was used for pH determination. Inductively coupled plasma (ICP) studies were carried out on Varian VISTA-PRO CCD, Australia

Fabrication of ZnO Nanoparticles

The manufacture of ZnO nanoparticles is pursued from an in-house procedure as follows. To a solution of Zinc nitrate hexahydrate (0.02 mol) in 50 ml of double-distilled water ascorbic acid (0.04 mol) and glycerol (0.04 mol) were added subsequently. The resulting solution was refluxed at 80 °C for 2 h. After that, the sol is obtained slowly heated at 70 °C for 2 h in an open bath until a wet gel was received. Finally, the wet gel was thoroughly dried by direct heating on a hot plate at 100 °C for 2 h. The resultant product was black powder. Then it was calcined in a furnace at 500 °C for 2 h at a rate of 5 °C min⁻¹, and ZnO nanoparticles with a white color were obtained (Fig. 1). The temperature of calcination was chosen based on thermogravimetric analysis (TGA), as shown in Fig. 2. The results showed that 500 °C was an optimum calcinations temperature for the
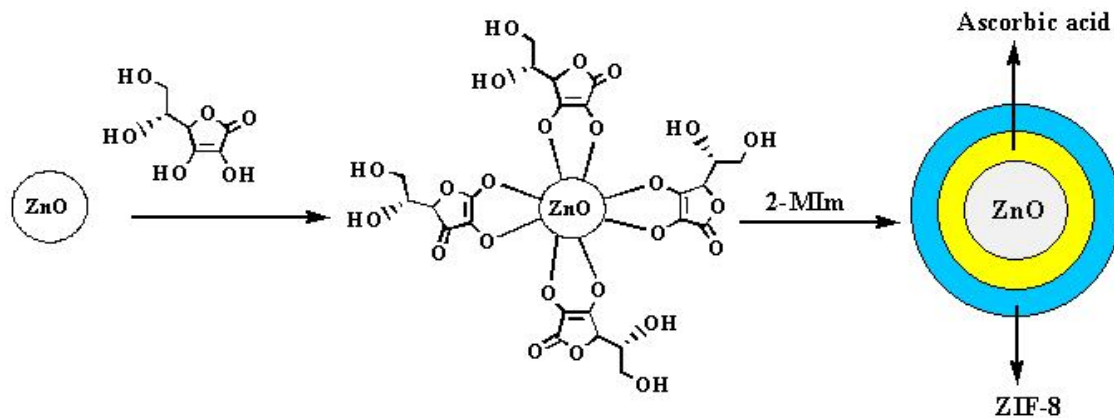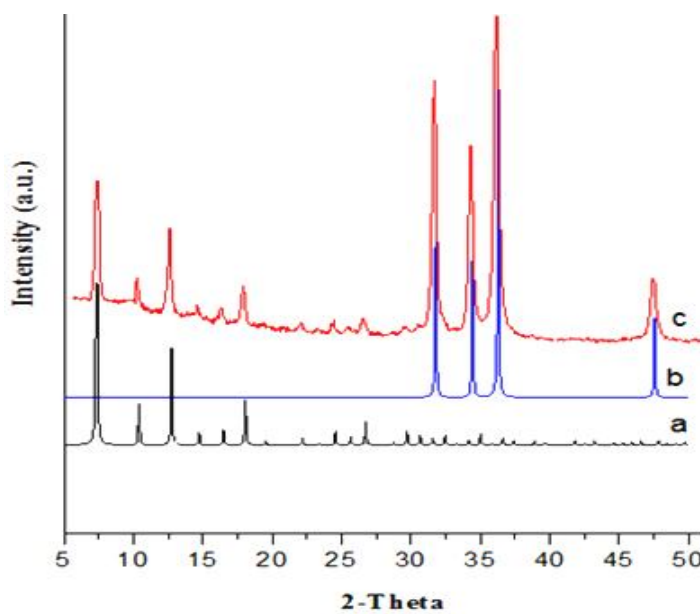
Scheme 1. Schematic representation of the procedure for the fabrication of the ZnO@AA/ZIF-8 nanohybrid
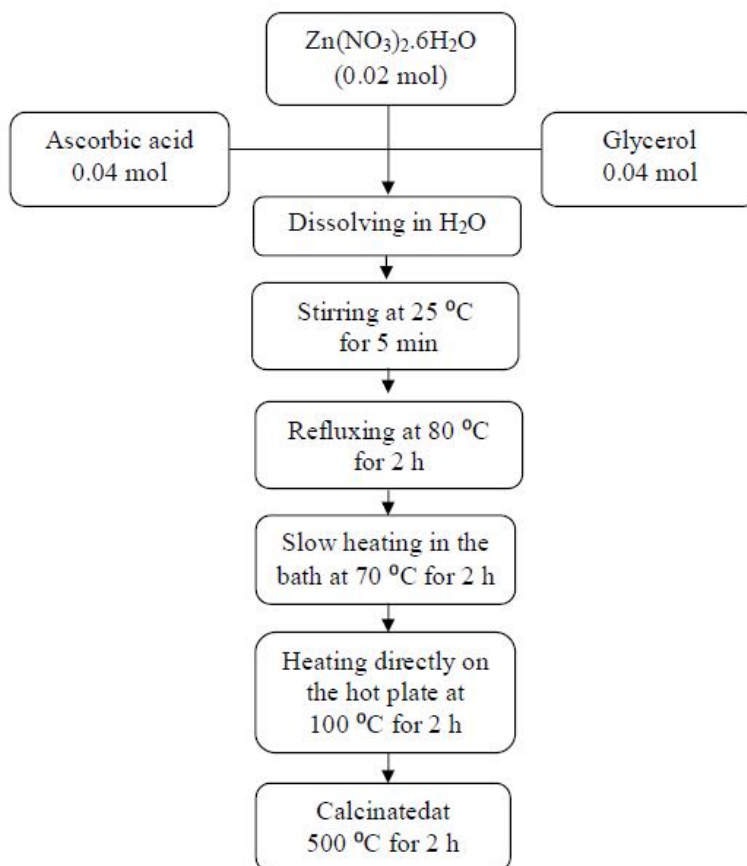
Fig. 1. The flow chart for preparation of ZnO nanospheres.
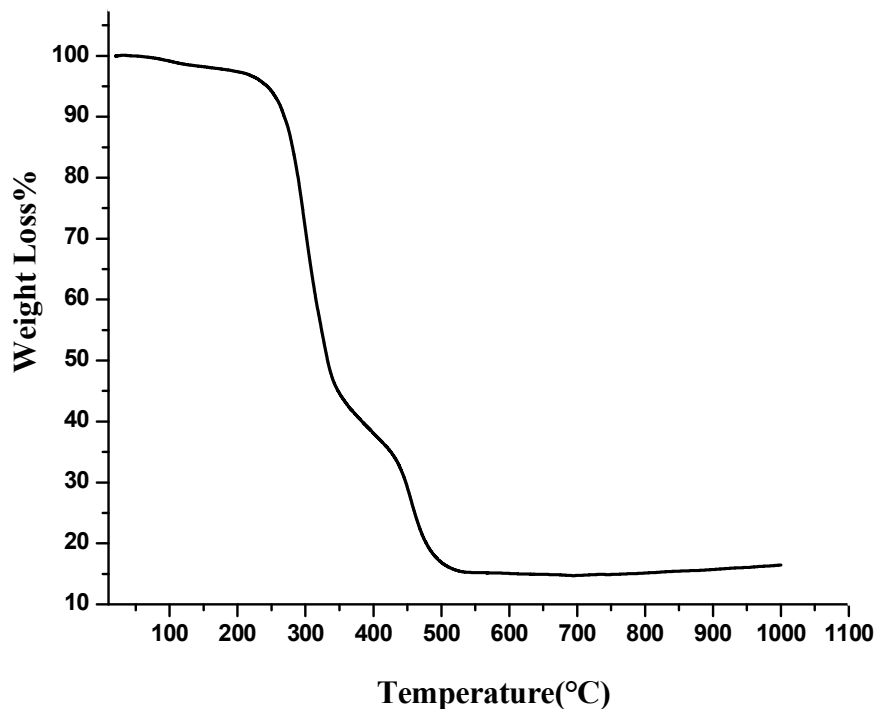
Fig. 2. The TGA curve for as-synthesized ZnO nanoparticles.

Fig. 3. XRD patterns of ZnO@AA/ZIF-8 nanohybrid (c) in comparison with the standard patterns of ZIF-8 (a) and ZnO (b) simulated using Mercury software.

manufactured of ZnO nanopowders (Fig. 2).

Preparation of ZnO@AA Nanoparticles

To 0.5 g ZnO nanoparticles, 30.0 ml of aqueous solutions of ascorbic acid (at pH near neutral) was added, and the reaction mixture was stirred at room temperature for 5 h. Afterward, the product was centrifuged and washed with water. Finally, ZnO_2@AA nanohybrid was obtained after drying for 4 h at 80 °C.

Preparation of the Core-coronal-shell ZnO@AA/ZIF-8 Nanohybrid

At first, a solution of 2-methylimidazole in ethanol (80.5 mmol) was prepared. Then, 0.5 g of ZnO_2@AA nanohybrid was added to this solution slowly. The resulting mixture was stirred at room temperature for 24 h. Afterward, the product was centrifuged and washed with ethanol. Finally, the ZnO@AA/ZIF-8 nanohybrid was obtained after drying for 4 h at 80 °C in a vacuum oven (Scheme 1).

RESULTS AND DISCUSSION

Characterization of the ZnO@AA/ZIF-8 Nanohybrid

The XRD patterns are shown in figure 3to confirm the successful synthesis of ZnO@AA/ZIF-8 nanohybrid (Fig. 3c). The prominent peaks observed (Fig. 3b) at $2\theta = 31.80, 34.41, 36.21, 47.52$ were assigned to the ZnO structure, which is in agreement with the XRD pattern reported in the literature [3-6]. The other diffraction peaks observed (Fig. 3a) at $2\theta = 7.28, 10.24, 12.74$ were assigned to the ZIF-8 structure which is in agreement with the XRD pattern simulated from the *sod*-type single crystal data (using Mercury Software) and reported in the literature [8-11].
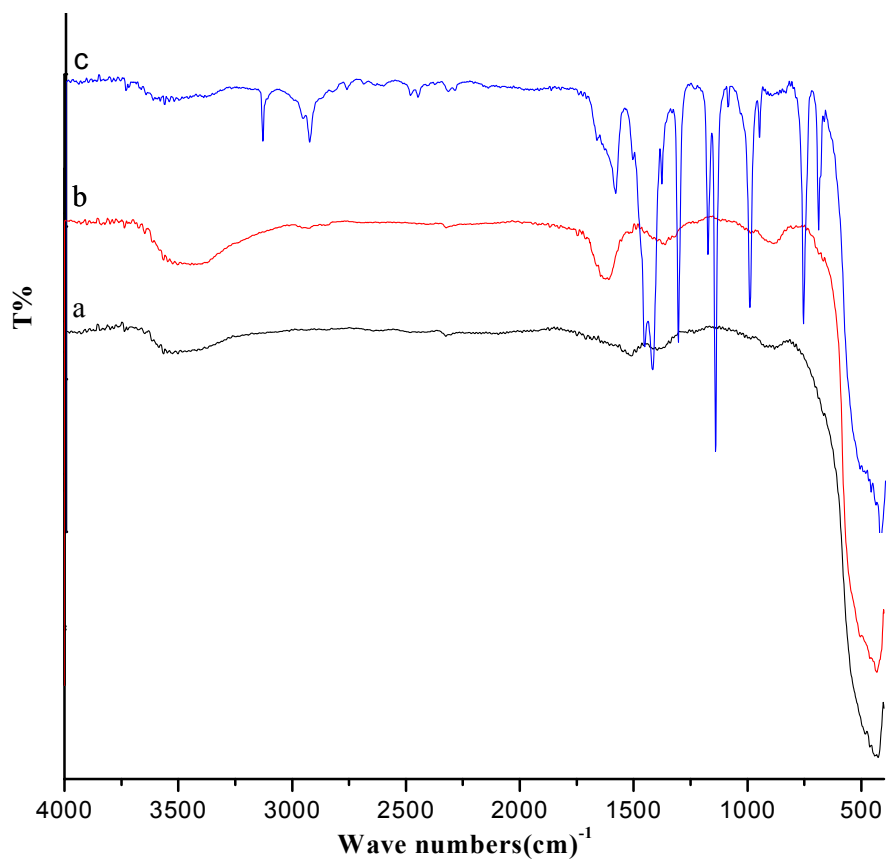
The FT-IR spectra of ZnO, ZnO/AA and ZnO@AA/ZIF-8 nanohybrid have been depicted in Fig. 4. The FT-IR spectrum of ZnO nanoparticles (Fig. 4a) reveals that the presence of the bands at 3135 and 1511 cm^{-1} are attributed to the stretching and bending vibrations of the OH groups on the surface of ZnO nanoparticles, respectively. The major band at 422 cm^{-1} is attributed to the stretching vibration of Zn-O group [8-11]. Figure 4b shows the

successful synthesis of ZnO/AA compound. Hydroxyl groups of furan ring binding to AA react with OH groups on the surface of ZnO nanoparticles. The appearance of peaks in the range of 898 and 987 cm^{-1} rationalized to C-O stretching vibration of Zn-O-C. The characteristic bands of the presence of ascorbic acid were found at 1631 cm^{-1} (C=O) and 1500 cm^{-1} (C=C), shows the existence of the ascorbic acid on the surface of ZnO/AA nanocomposite [15]. Figure 4c confirms the successful fabrication of core-coronal-shell ZnO/AA@ZIF-8 nanohybrid. The bands at 3400 and 2929 cm^{-1} are ascribed to the aromatic and the aliphatic C-H stretch of the imidazole, respectively. The major band at 1584 cm^{-1} which are attached to the stretching vibration of C=N group. The peaks at 600-1500 cm^{-1} correspond to the entire ring stretching or bending, and the band at 421 cm^{-1}corresponds to the Zn-N group present in the ZIF-8 structure [8-11].

Moreover, the dispersive energy spectrum (EDS) (Fig. 5) reveals that the presence of C, Zn, N, O elements in the ZnO@AA/ZIF-8 nanohybrid. This analysis confirms the successful formation of the ZnO/AA@ZIF-8 nanohybrid. Information about the morphology of the ZnO/AA@ZIF-8 nanohybrid was directly obtained through SEM *analysis*. As it's been shown in Fig. 6, SEM images demonstrate that the ZIF-8 is relatively good distributed around the ZnO surface. Comparison of these images (a and b) indicates that ZIF-8 has been more effectively composed around the ZnO surface during the reaction. Moreover, Fig. 6a confirms the formation of ZnO nanospheres.

GENERAL PROCEDURE FOR REMOVAL OF As(V)

After successful synthesis of the core-coronal-shell ZnO@ZIF-8 nanohybrid, its application for removal of arsenic (As(V)) was evaluated in a batch reactor system. Arsenic removal experiments through the adsorption process were carried out in a batch stirred tank equipped with heating apparatus. For this purpose, 0.05 g of the desired adsorbent was used for 50 ml solution of arsenic. The other important variables affecting the adsorption of arsenic, including pH, initial concentration, temperature, and contact time were determined constant at neutral, 10 ppm, 25 °C and 60 min, respectively. Furthermore, the stirring speed was kept constant around 200 rpm for all
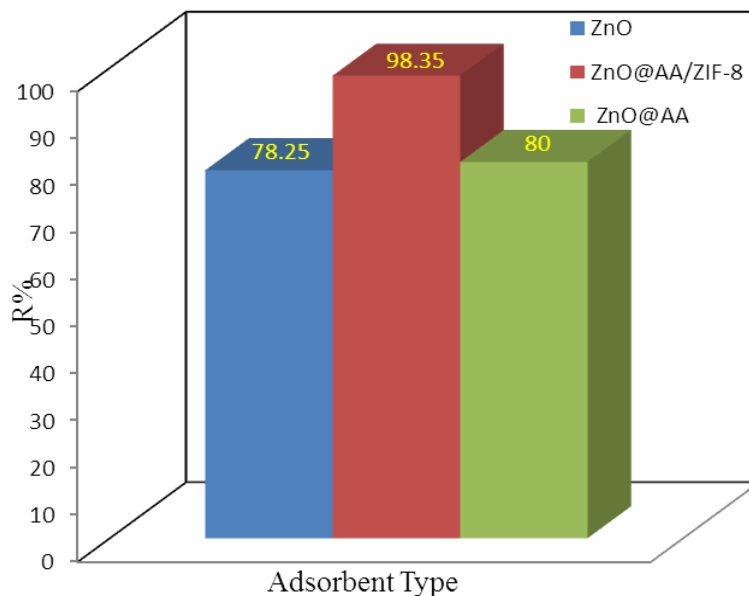
Fig. 4. FT-IR spectra of the ZnO (a), ZnO/AA (b) and ZnO@AA/ZIF-8 (c).
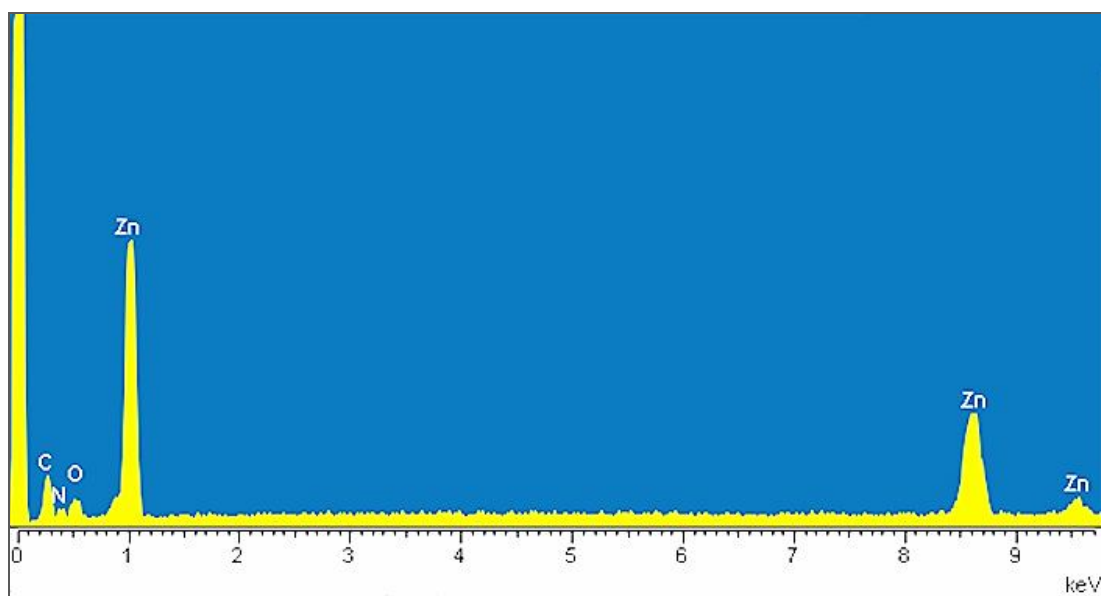
Fig. 5. EDX analysis of the ZnO@AA/ZIF-8nanohybrid.
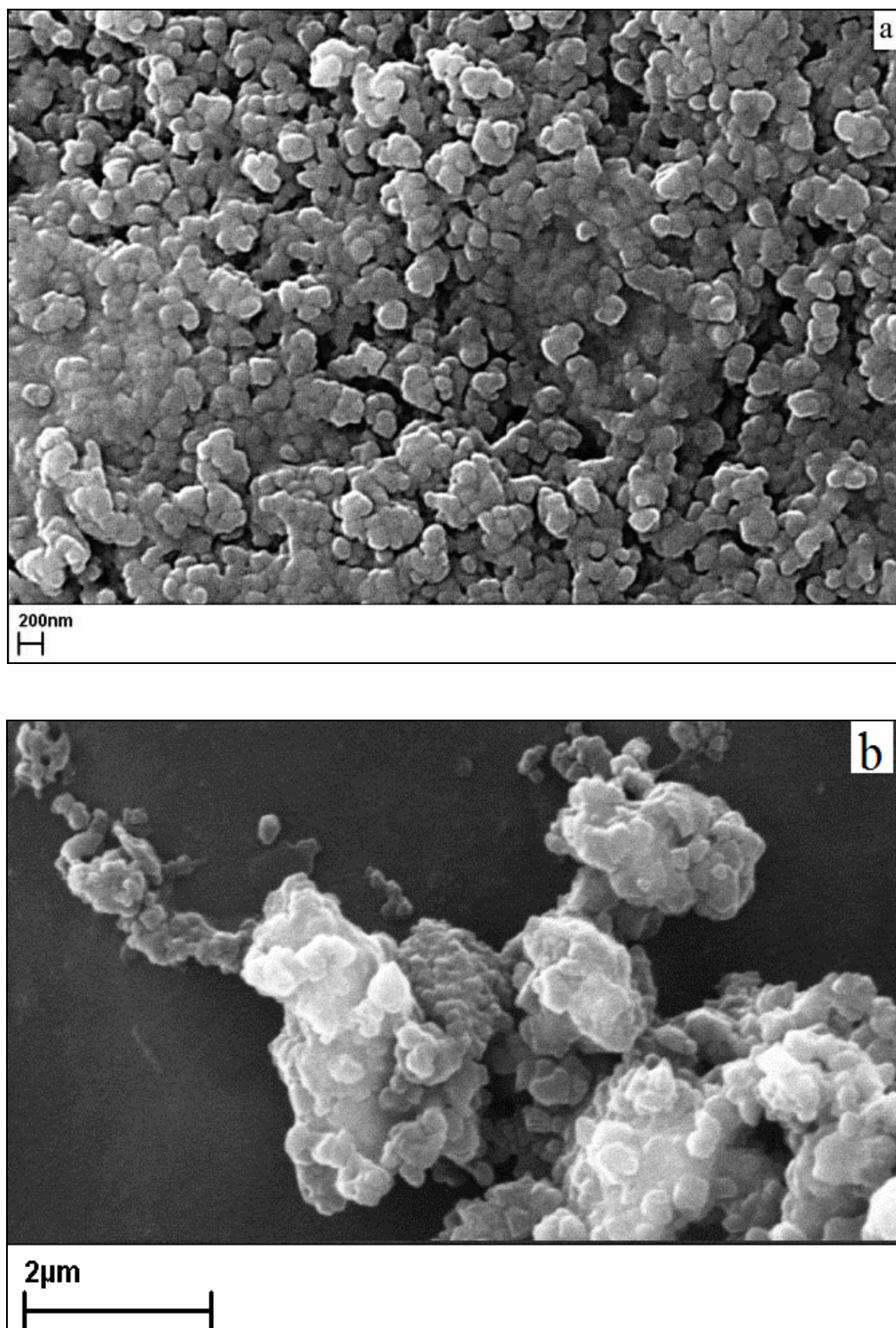
Fig. 6. SEM images of ZnO (a) and ZnO@AA/ZIF-8 (b).

Fig. 7. Comparison of removal efficiency (R%) of As(V) on the ZnO@AA/ZIF-8 with ZnO@AA and ZnO at the same conditions (adsorbent dosage = 0.05 g, initial concentration = 10 ppm, pH = 7, T = 25 °C, t = 60 min).

experiments. After that time, the adsorbent was centrifuged and separated, and the solution was evaluated for arsenic concentration determination through ICP analysis. The obtained results reveal that the high efficiency of ZnO@AA/ZIF-8 adsorbent in As(V) removal compared to pristine ZnO. While the concentration of As(V) in the solution after mixing with ZnO nanospheres is measured around 2.175 ppm, this value was obtained 0.165 ppm for ZnO@AA/ZIF-8 (see supporting information). These results demonstrate the success of specific affinity and surface area enhancement of ZnO using ascorbic acid functional group and ZIF-8, respectively.

The arsenic removal efficiency was also calculated *via* following equation.

$$R\% = \frac{C_0 - C_e}{C_0} \tag{1}$$

Where C_0 and C_e are defined as initial and final concentration of arsenic in solution (mg l^{-1}), respectively. Figure 7 shows the calculated removal efficiency of the arsenic using pristine ZnO and ZnO@AA in comparison with ZnO@AA/ZIF-8 nanohybrid at the same conditions (Fig. 7).

CONCLUSIONS

In summary, the ZnO@AA/ZIF-8 nanohybrid prepared by interaction of 2-methylimidazole with ZnO coated with ascorbic acid and employed to removal of As(V) ions from water. The morphology and composition were characterized by a variety of technological means to confirm the structure of synthesized ZnO@AA/ZIF-8. It was observed that the removal efficiency of the arsenic using ZnO@AA/ZIF-8 nanohybrid was around 25% higher than that for ZnO and ZnO@AA components. Additionally, the use of ascorbic as a ''green'' agent, both as a complexing agent for ZnO synthesis and as a safe and economic linker for fabrication of ZnO@AA/ZIF-8 nanohybrid as well as easy and safe procedures are cost-effective, environmentally benign, which makes title methodologies suitable for removal of various of heavy ions from groundwater.

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